Synthesis and Structural Analysis of a Homogeneous Series of Anhydrous Rare-earth-metal Perchlorates†

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The reaction of Cl_2O_6 with anhydrous or hydrated metal(III) chlorides, nitrates or hydrated perchlorates leads to anhydrous metal perchlorates $M(ClO_4)_3$ (M = Y, La, Nd, Sm, Gd or Er). The complexes are isostructural and crystallise in the monoclinic system (space group $P2_1/m$): $8.219(6) < a < 8.384(6)$, $5.602(1) < b < 5.869(9)$, $7.329(4) < c < 7.481(2)$ Å, $102.88(4) < \beta < 104.09(5)°$, $328.957 < U < 357.110$ Å^3. Vibrational spectroscopic data show a bridging tridentate co-ordination of ClO_4, and a polymeric layered structure, derived from that of UCl_3, is suggested. Intense fluorescence of Er^{3+} in the $Er(ClO_4)_3$ complex has been observed. The synthesis and characterisation of three salts, $(NO_2)_3Er(ClO_4)_6$, $ClO_2Er(ClO_4)_4$ and $(ClO_2)_{0.33}La(ClO_4)_{3.33}$, are also described.

Much research in the area of the systematic synthesis and characterisation of anhydrous perchlorato complexes of elements in Mendeleev's classification has been performed[1–21] since 1961, with the initial work by Hathaway and Underhill[1] on iron and copper perchlorates and the subsequent discovery of Cl_2O_6 as a highly efficient perchlorating reagent.[3,11] Although the information available on these complexes has considerably increased, some areas remain unexplored and work continues today.[20]

Recent research on scandium perchlorato complexes[19] completed the first transition-metal series and began studies of the rare-earth-metal family. As shown by infrared and Raman spectroscopies, the molecular structure of $Sc(ClO_4)_3$ is analogous to that of $Ga(ClO_4)_3$, in which the ClO_4 groups are bridging bidentate.[6] Although the complexes crystallise differently [$Ga(ClO_4)_3$, hexagonal $R\bar{3}$; $Sc(ClO_4)_3$, tetragonal], the chemical properties of the chloryl salt $(ClO_2)_{0.25}Sc(ClO_4)_{3.25}$ nevertheless suggest a layered structure for $Sc(ClO_4)_3$ similar to that of $Ga(ClO_4)_3$.

Anhydrous perchlorato complexes of lanthanide ions were prepared some years ago,[6,7] however, to the best of our knowledge, the literature does not report any structural information on perchlorato complexes in which the central atom is unsolvated by water or an organic solvent. Their synthesis depends on a dehydration process or a way of removing the solvent of solvated complexes. It is well known that this method of preparation leads sometimes to oxo, hydroxo or incompletely dehydrated complexes[8] and presents great safety hazards when the solvent is an organic base.

Previous studies have shown that the best perchlorating and dehydrating reagent is Cl_2O_6,[3,8,11] which was therefore used in this work to synthesise perchlorato complexes of yttrium, lanthanum, neodymium, samarium, gadolinium and erbium using hydrated or anhydrous chlorides, hydrated perchlorates or nitrates as starting materials. A first structural approach is described using infrared and Raman spectroscopic and X-ray powder diffraction data.

Experimental

CAUTION: Cl_2O_6 and perchlorates are highly explosive compounds particularly on contact with organic substances and under shock. They must be handled with care. Reactions must be continuously monitored and, because of their hygroscopicity, products must be handled in a glove-box filled with extra-dry nitrogen or argon, or in a vacuum line.

Materials.—The compound Cl_2O_6 was prepared at −10 °C by oxidising ClO_2 in a stream of O_3/O_2 (8% in O_3).[11] Chlorine dioxide was usually synthesised at 50 °C by reducing ClO_3^- ($KClO_3$, Merck for analysis) with $H_2C_2O_4 \cdot 2H_2O$ (Merck for analysis) in a 2.5 mol dm^{-3} H_2SO_4 solution. It was passed over P_2O_5 before use. Chlorine trioxide Cl_2O_6 is often polluted with CO_2, ClO_2 and $HClO_4$ and then appears as a blood-red liquid. Impurities were removed by a trap-to-trap distillation (+10 °C to −20 °C). Pure Cl_2O_6 was collected at −20 °C as very beautiful ruby-like crystals; 25 g of $KClO_3$ and 8 h of reaction yield 8–10 g of Cl_2O_6.

The origin and purity of the starting compounds with which Cl_2O_6 was treated are given in Table 1.

General Method of Synthesis.—The vacuum line in which the synthesis of the perchlorato complexes was performed has been described elsewere.[11] The general procedure, as well as the purification of the complexes and their decomposition, follows that given in previous papers.[3,8,11] In a typical reaction, successive additions of Cl_2O_6 (2–4 g) were made at −180 °C to chlorides, hydrated perchlorates or nitrates (0.3–1 g). The mixture was slowly warmed to room temperature and continuously stirred. Evolved gases were periodically evacuated throughout the reaction. Excess of Cl_2O_6 was pumped out under vacuum (10^{-2} Torr) at the end of the reaction.

Chemical Analysis.—Water was added to perchlorate samples at −180 °C and the mixtures were slowly warmed (12 h) to room temperature before analysis. The ions Y^{III}, La^{III}, Nd^{III}, Sm^{III}, Gd^{III} and Er^{III} were analysed by a complexometric method using a 0.05 mol dm^{-3} ethylenediaminetetraacetate solution (Titriplex III, Merck) in a slightly acidic medium (pH 6).[22] The end-point of the titration was determined with xylene orange as indicator. Perchlorate was analysed by a potentiometric method with an Orion specific electrode and a 0.04 mol dm^{-3} tetraphenylarsonium solution (Merck for analysis) as titrant.[23]

Structural and Spectroscopic Analysis.—X-Ray diffraction

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† *Non-SI unit employed:* Torr ≈ 133 Pa.

patterns were obtained using Cu-Kα radiation on an automatised Philips PW 1965/30 goniometer.[24] Powders were held on an aluminium plate protected with a beryllium window (0.015 mm thick). Infrared spectra were recorded on a BOMEM DA8 FTIR spectrometer on samples of perchlorates pressed between silicon plates [(111) cleavage, thickness 1 mm]. Raman spectra were collected at room temperature on a DILOR spectrometer linked to a PC computer and using a Spectra Physics argon laser (5145 or 4880 Å lines and 0.2 W). In order to avoid an intense fluorescence some Raman spectra, those of erbium complexes for instance, were obtained using a YAG CVI laser (10640 Å) on the above FTIR instrument. Sampling was generally made into a Pyrex tube (outside diameter 8 mm). Fluorescence spectra of $Er(ClO_4)_3$ were obtained with the exciting line at 488 nm ($^4I_{\frac{15}{2}} \longrightarrow {}^4F_{\frac{7}{2}}$). Sampling and manipulation were identical to those employed for Raman spectroscopy.

Results and Discussion

Synthesis of Anhydrous Perchlorates.—Details, as well as analytical data, are reported in Table 1.

From metal chlorides. (*a*) *Anhydrous chlorides.* Using anhydrous MCl_n ($NdCl_3$) as starting material, the usual, now well known, synthetic route can be written as in equations (1)–(3).

$$MCl_n + (m + n)Cl_2O_6 \longrightarrow ClO_2M(ClO_4)_{n+1}{\cdot}(m - 1)Cl_2O_6 + nClO_2 + \tfrac{n}{2}Cl_2 \quad (1)$$

$$ClO_2M(ClO_4)_{n+1}{\cdot}(m - 1)Cl_2O_6 \xrightarrow{-20\ °C,\ \text{vacuum}} ClO_2M(ClO_4)_{n+1} + (m - 1)Cl_2O_6 \quad (2)$$

$$ClO_2M(ClO_4)_{n+1} \xrightarrow{\text{increasing temperature, vacuum}} M(ClO_4)_n + Cl_2O_6 \quad (3)$$

(*b*) *Hydrated chlorides.* From $GdCl_3{\cdot}6H_2O$ and $ErCl_3{\cdot}6H_2O$, the complete steps described above were only observed for the latter, from which a chloryl salt could be isolated. It lost Cl_2O_6 above 70 °C to give $Er(ClO_4)_3$.

$$MCl_n{\cdot}mH_2O + nCl_2O_6 \longrightarrow M(ClO_4)_n{\cdot}mH_2O + \tfrac{n}{2}Cl_2 + nClO_2 \quad (4)$$

$$M(ClO_4)_n{\cdot}mH_2O + mCl_2O_6 \longrightarrow M(ClO_4)_n + mHClO_3 + mHClO_4 \quad (5)$$

$$M(ClO_4)_n + xCl_2O_6 \longrightarrow (ClO_2)_xM(ClO_4)_{n+x}\ (x < 1) \quad (6)$$

$$(ClO_2)_xM(ClO_4)_{n+x} \xrightarrow{\text{heat}} M(ClO_4)_n + xCl_2O_6 \quad (7)$$

The chloryl salts of neodymium and gadolinium could not be isolated at room temperature, as found also for divalent cadmium or mercury complexes.[17] This can be explained by the initial formation of the double salt $M(ClO_4)_n{\cdot}Cl_2O_6$, Cl_2O_6 being included at low temperature between the layers of $M(ClO_4)_n$ and removed easily by pumping at room temperature.

A previous study on the differences in the reactivities of anhydrous or hydrated metal chlorides toward Cl_2O_6 has shown that hydrated chlorides react more quickly. Possible explanations for this phenomenon (compactness of the lattice, molecular geometry at the hydrated metal ion) are given elsewhere.[8] However, in the present case no difference was observed between the reactivities of anhydrous $NdCl_3$ and other hydrated rare-earth-metal chlorides, as previously reported for $FeCl_3{\cdot}nH_2O$ ($0 < n < 9$).[15]

From oxides. It has been shown that it is difficult to induce oxides to react with Cl_2O_6[8] and therefore the general pathway in equations (8)–(10) was adopted. The perchlorates of Y, La, Sm and Er could be prepared in this way.

$$MO^{\frac{n}{2}} + nHClO_4 \xrightarrow[\text{(stirring and boiling)}]{\text{aqueous solution}} M(ClO_4)_n{\cdot}m'H_2O \quad (8)$$

$$M(ClO_4)_n{\cdot}m'H_2O \xrightarrow{\text{heat}} M(ClO_4)_n{\cdot}mH_2O\ (m < 6) \quad (9)$$

$$M(ClO_4)_n{\cdot}mH_2O + mCl_2O_6 \longrightarrow \text{steps (5)–(7)} \quad (10)$$

However, as observed for Nd^{III} and Gd^{III} (and for the same reason), it was not possible to isolate chloryl salts of Y^{III} and Sm^{III} at room temperature. When Cl_2O_6 was treated with $M(ClO_4)_3{\cdot}nH_2O$ (M = La or Er) two chloryl salts, $ClO_2Er(ClO_4)_4$ and $(ClO_2)_{0.33}La(ClO_4)_{3.33}$, were isolated.

Table 1 Synthetic and analytical data for rare-earth-metal perchlorato complexes

Reagents		Reaction products	Colour	Analysis (%)[a]		
				M	ClO_4	ClO_2
$NdCl_3$[b]	Cl_2O_6[c]	$Nd(ClO_4)_3$	Yellow-orange	33.70 (32.35)	66.25 (67.65)	
$GdCl_3{\cdot}6H_2O$[d]	Cl_2O_6	$Gd(ClO_4)_3$	White	34.85 (34.50)	65.15 (65.50)	
$ErCl_3{\cdot}6H_2O$[e]	Cl_2O_6	$ClO_2Er(ClO_4)_4$	Yellow	25.70 (25.60)	60.05 (60.95)	14.30 (13.40)
$ClO_2Er(ClO_4)_4$	Heat	$Er(ClO_4)_3$	White-yellow	36.35 (35.95)	63.65 (64.05)	
Y_2O_3[f]	$HClO_4$, 72%[g]	$Y(ClO_4)_3{\cdot}nH_2O$	White-yellow		*h*	
$Y(ClO_4)_3{\cdot}nH_2O$	Cl_2O_6	$Y(ClO_4)_3$	Yellow	22.65 (22.95)	77.30 (77.05)	
La_2O_3[i]	$HClO_4$, 72%	$La(ClO_4)_3{\cdot}nH_2O$	Yellow		*h*	
$La(ClO_4)_3{\cdot}nH_2O$	Cl_2O_6	$(ClO_2)_{0.33}La(ClO_4)_{3.33}$	Orange	28.15 (28.20)	67.30 (67.25)	4.55 (4.55)
$(ClO_2)_{0.33}La(ClO_4)_{3.33}$	Heat	$La(ClO_4)_3$	Orange	32.30 (31.75)	67.70 (68.25)	
Sm_2O_3[j]	$HClO_4$, 72%	$Sm(ClO_4)_3{\cdot}nH_2O$	White		*h*	
$Sm(ClO_4)_3{\cdot}nH_2O$	Cl_2O_6	$Sm(ClO_4)_3$	White	33.50 (33.50)	66.50 (66.50)	
Er_2O_3[k]	$HClO_4$, 72%	$Er(ClO_4)_3{\cdot}nH_2O$	Pink		*h*	
$Er(ClO_4)_3{\cdot}nH_2O$	Cl_2O_6	$ClO_2Er(ClO_4)_4$	Yellow	25.70 (25.60)	60.05 (60.95)	14.30 (13.40)
$ClO_2Er(ClO_4)_4$	Heat	$Er(ClO_4)_3$	White-yellow	35.90 (35.95)	64.10 (64.05)	
Er_2O_3	HNO_3, 100%[l]	$Er(NO_3)_3{\cdot}nH_2O$ ($n = 2.5$)	Pink		*h*	
$Er(NO_3)_3{\cdot}nH_2O$ ($n = 2.5$)	Cl_2O_6	$(NO_2)_3Er(ClO_4)_6$	White-yellow	35.90 (35.95)	64.10 (64.05)	15.30 (15.3)[m]

[a] Required values are given in parentheses. [b] K & K international corporation (99.9% pure). [c] See text. [d] Prolabo rectapur. [e] Aldrich (99.9%). [f] Fluka (99.98%) [g] Labosi analypur. [h] As deduced from weighing, and IR and Raman data. [i] Labosi pure. [j] Prolabo rectapur. [k] Alpha Ventron (99.999%). [l] Merck. [m] NO_2.

Their thermal decomposition led to $M(ClO_4)_3$ (M = Er or La) complexes at 70 and 65 °C respectively under vacuum (10^{-2} Torr).

From hydrated nitrates. The identification of a chloryl salt allowed the existence of other salts of erbium, such as a nitryl salt for example, to be envisaged, and the reaction of Cl_2O_6 with an erbium nitrate was therefore studied. The salt $Er(NO_3)_3{\cdot}2.5H_2O$ was used as starting material, obtained by controlled evaporation of a solution of Er_2O_3 in HNO_3 (100%). As previously observed[8] for other metals, the final product resulting from the addition of Cl_2O_6 to this hydrated nitrate was a nitryl perchlorate complex: $(NO_2)_3Er(ClO_4)_6$. Here, dehydration and perchlorate formation occur simultaneously unlike the reaction with chlorides. The general pathway of the synthesis, given in detail elsewhere,[8] can be summarised as in equations (11)–(13). The reaction (12) must be performed at 0 °C in order to prevent decomposition of the nitryl complex and the formation of a chloryl salt. $(NO_2)_3Er(ClO_4)_6$ decomposes at 145 °C under vacuum (10^{-2} Torr) to give NO_2ClO_4 condensed on the wall of the reactor and $NO_2Er(ClO_4)_4$.

$$MO_{\frac{n}{2}} + nHNO_3 \xrightarrow[\text{(stirring and boiling)}]{\text{aqueous solution}} M(NO_3)_n{\cdot}mH_2O \quad (11)$$

$$M(NO_3)_n{\cdot}mH_2O + (2n + m)Cl_2O_6 \longrightarrow (NO_2)_nM(ClO_4)_{2n} + 2nClO_2 + \tfrac{n}{2}O_2 + mHClO_3 + mHClO_4 \quad (12)$$

$$(NO_2)_nM(ClO_4)_{2n} \xrightarrow{\text{heat}} (NO_2)_{n-x}M(ClO_4)_{2n-x} + xNO_2ClO_4 \quad (13)$$

We note the high decomposition temperature of this nitryl salt compared to that generally observed (below 115 °C). A similar temperature was reported for $(NO_2)_2Ni(ClO_4)_4$.[8]

Structural and Spectroscopic Analysis.—Bünzli and Kasparek[25] used Fourier-transform IR and fluorescence spectroscopies in order to study the co-ordination and solvation sphere of lanthanide(III) ions in perchlorato complexes dissolved in anhydrous solvents, but did not report any structural information on covalent unsolvated perchlorates. In view of the poor crystallisation properties and the difficulties inherent in single-crystal growth of perchlorato complexes, structural information can only be obtained from X-ray diffraction on powders and from vibrational (infrared and Raman) spectroscopy.

X-Ray diffraction. The X-ray powder data for the $M(ClO_4)_3$ complexes (M = Y, La, Nd, Sm, Gd or Er) are given in Table 2. In spite of the poor quality of the spectra of $Nd(ClO_4)_3$ and $La(ClO_4)_3$, indexation of lines shows that the complexes are isostructural and that they crystallise in the monoclinic system.

Except for yttrium and erbium chlorides (monoclinic, $AlCl_3$, space group $C2/m$), the structure of the other rare-earth-metal chlorides (La, Nd, Sm and Gd) are related to that of UCl_3 (hexagonal system, $P6_3/m$). In all cases, the metal atoms are arranged to form layers. Previous results on perchlorato complexes had shown that their structure often derives from the parent chloride, although the volume and the geometry of the perchlorate group induce a loss of symmetry. We have related the structure of $M(ClO_4)_3$ complexes (M = Y, La, Nd, Sm, Gd or Er) to that of UCl_3 since the nine-co-ordination of the atoms appears both in this chloride[26] and in the perchlorato complexes (see spectroscopic results below).

The X-ray data for the chloryl and nitryl salts are reported in Table 3. In view of their complexity, particularly those of the erbium salts, indexation was not attempted, but comparison of the data for the two salts allows the following conclusions. Some lines appear at very similar angles in the two spectra, and it is suggested that they belong to an $AM(ClO_4)_4$ species (with A = ClO_2 or NO_2). The extra lines, and in particular some intense lines in the spectrum of $(NO_2)_3Er(ClO_4)_6$, can be assigned to NO_2ClO_4, according to the literature,[14] such that $(NO_2)_3Er(ClO_4)_6$ can be written as a double salt $NO_2Er(ClO_4)_4{\cdot}2NO_2ClO_4$. Similar results have been found with other nitryl salts,[8] and are not surprising since definite compounds $(NO_2)_nM(ClO_4)_{2n}$ are rarely obtained in a first step when Cl_2O_6 reacts with a metal nitrate.[17]

Vibrational spectroscopy. (*a*) $M(ClO_4)_3$ (M = Y, La, Nd, Sm, Gd *or* Er). Infrared and Raman spectra of these complexes are shown in Fig. 1. They are very similar and this suggests the same co-ordination mode of ClO_4 groups around the metal. The spectra are absolutely different from those of $Sc(ClO_4)_3$, in which the perchlorate groups are bridging bidentate,[19] but the line and band frequencies, and their shape, agree with those of $Ce(ClO_4)_3$[18] or $M(ClO_4)_2$ (M = Mn, Co, Ni, Zn or Cd)[10,11,16,17] in which the ClO_4 groups are bridging tridentate.

The broad IR band between 1000 and 1100 cm^{-1}, with two corresponding weak lines in the same range in the Raman, and the sharper absorption around 970 cm^{-1} (very strong at 990 cm^{-1} in the Raman) are characteristic of the stretching vibrations $\nu_{sym}(ClO_b)$ (A_1) and $\nu_{asym}(ClO_b)$ (E) (O_b = bridging oxygen) of a C_{3v} tridentate perchlorate group.[8] Given the

Table 2 X-Ray powder data (*d* in Å) for $M(ClO_4)_3$ complexes (M = Y, La, Nd, Sm, Gd or Er)

$Y(ClO_4)_3$			$La(ClO_4)_3$			$Nd(ClO_4)_3$			$Sm(ClO_4)_3$			$Gd(ClO_4)_3$			$Er(ClO_4)_3$			
I/I_0	d_{obs}	d_{calc}	I/I_0	d_{obs}	d_{calc}	I/I_0	d_{obs}	d_{calc}	I/I_0	d_{obs}	d_{calc}	I/I_0	d_{obs}	d_{calc}	I/I_0	d_{obs}	d_{calc}	*h k l*
			50.2	4.72	4.76	16.7	4.80	4.70	37.1	4.67	4.65	37.9	4.67	4.64	53.3	4.61	4.60	1 1 0
77.8	3.58	3.60	72.6	3.56	3.62	14.3	3.63	3.62	47.9	3.62	3.60	58.7	3.61	3.60	64.8	3.57	3.58	0 0 2
100	3.27	3.28	79.5	3.35	3.34	18.3	3.32	3.31	100	3.30	3.29	100	3.29	3.28	100	3.26	3.27	2 1 0
			69.0	3.10	3.10													−2 0 2
54.8	3.03	3.03							33.9	3.04	3.04	32.1	3.04	3.04	47.6	3.02	3.02	0 1 2
27.4	2.82	2.82							14.2	2.88	2.85	19.2	2.87	2.84	47.7	2.80	2.80	0 2 0
45.9	2.67	2.68	65.1	2.75	2.72	15.8	2.70	2.69	73.5	2.69	2.69	70.0	2.68	2.68	79.8	2.66	2.67	3 0 0
			79.9	2.35	2.35													3 0 1
26.9	2.22	2.22				6.70	2.24	2.25	33.1	2.23	2.23	26.0	2.23	2.23	47.2	2.21	2.21	0 2 2
50.3	2.06	2.06				8.70	2.10	2.10	31.3	2.08	2.08	39.1	2.08	2.08	65.5	2.05	2.05	−2 2 2
			100	2.03	2.03	100	2.03	2.02										4 0 0

Space group	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
a/Å	8.242(8)	8.384(6)	8.281(6)	8.260(8)	8.257(6)	8.219(6)
b/Å	5.633(6)	5.869(9)	5.780(6)	5.703(3)	5.684(1)	5.602(1)
c/Å	7.354(6)	7.481(2)	7.441(4)	7.390(8)	7.391(6)	7.329(4)
β/°	102.94(2)	104.09(5)	103.04(6)	103.06(5)	103.03(1)	102.88(4)
U/Å^3	332.820	357.110	347.019	339.195	337.981	328.957

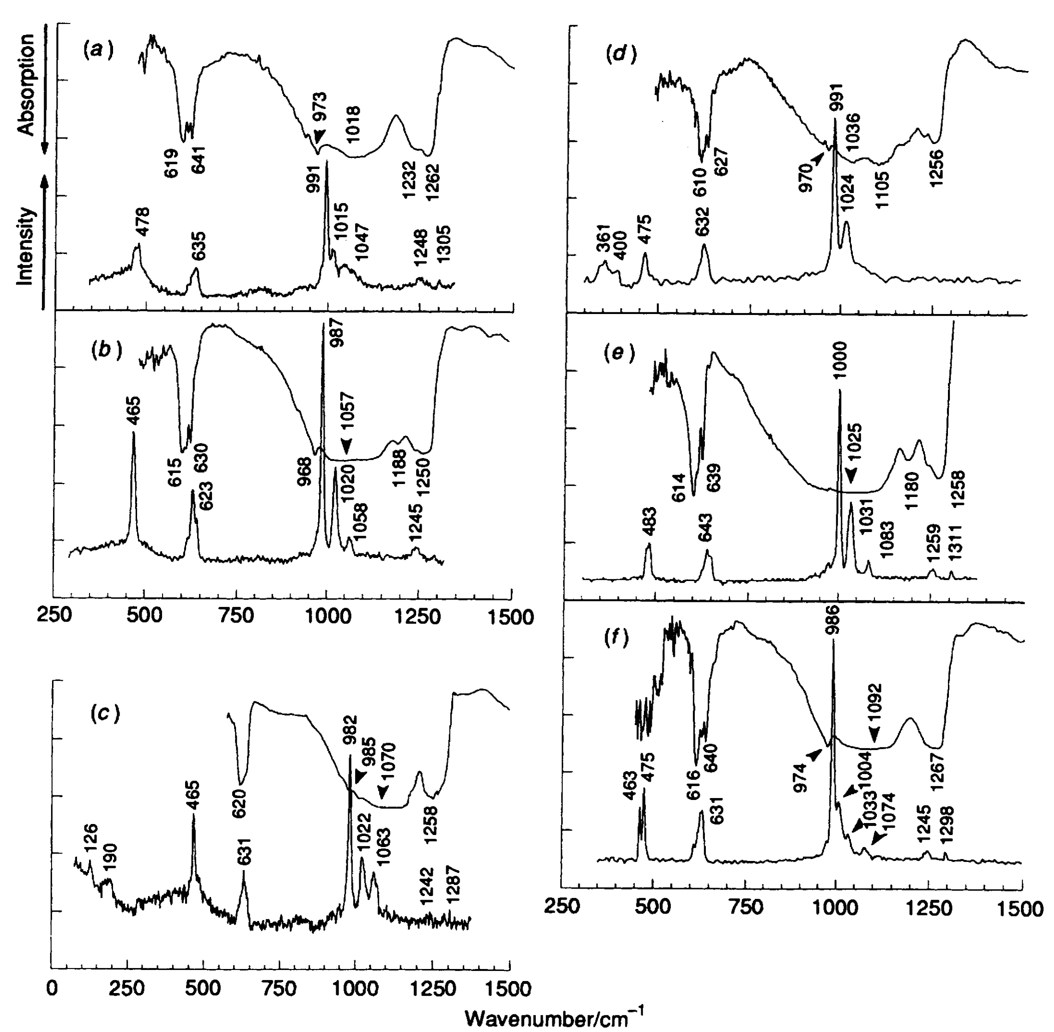

Fig. 1 Infrared and Raman spectra of $Y(ClO_4)_3$ (*a*), $Nd(ClO_4)_3$ (*b*), La $(ClO_4)_3$ (*c*), $Sm(ClO_4)_3$ (*d*), $Gd(ClO_4)_3$ (*e*) and $Er(ClO_4)_3$ (*f*)

Table 3 X-Ray powder data for $ClO_2Er(ClO_4)_4$ and $(NO_2)_3Er(ClO_4)_6$

$ClO_2Er(ClO_4)_4$		$(NO_2)_3Er(ClO_4)_6$	
I/I_0	d_{obs}/Å	I/I_0	d_{obs}/Å
58	4.67	50	4.66
		22	4.24[a]
65	4.08	29	4.09
68	3.87	33	3.89
		38	3.80[a]
		47	3.74[a]
		37	3.69[a]
100	3.64	51	3.64
		37	3.63[a]
89	3.59	81	3.59
85	3.42	70	3.42
83	3.35	100	3.37[b]
92	3.29		
76	3.20	46	3.21
80	3.16	30	3.13[b]
69	2.88	67	2.88
66	2.84		
66	2.75	40	2.75
71	2.69	38	2.55
		23	2.18
75	2.08	20	2.08

[a] From NO_2ClO_4. [b] From $AEr(ClO_4)_4$ (A = NO_2 or ClO_2) and NO_2ClO_4.

stoichiometry of the complexes and the bonding mode, a nine-co-ordination for the metal atom is deduced. The infrared frequencies observed for $\nu(ClO_t)$ (O_t = terminal oxygen), $1267 < \nu < 1250$ cm^{-1}, are in agreement with a weaker metal–perchlorate interaction than in $Ni(ClO_4)_2$ (1300 cm^{-1}) or $Co(ClO_4)_2$ (1278 cm^{-1}). This depends on the effective ionic radii and the electronegativity of the M^{n+} centre.

Deformation modes of perchlorate groups are usually assigned around 630 [$\delta_{asym}(ClO_b)$] and 470 cm^{-1} [$\delta_{sym}(ClO_b)$ and ρ_r (rocking)]. The weaker interaction $Me \cdots ClO_4$ is supported by a shift of $\delta_{asym}(ClO_b)$ of -15 to -35 cm^{-1} from its position observed for $Ni(ClO_4)_2$, 665 cm^{-1}. The ν(M–O) vibration can only be seen clearly for the $Sm(ClO_4)_3$ complex, where it is located in the broad line at 361 cm^{-1} in the Raman spectrum. The M–O distances, calculated from a relationship established elsewhere[21] [d(M–O) = $f(R)$ where R = Brown and Shannon effective ionic radii of the metallic centre[27]], decrease from 270 pm for La to 250 pm for Er, in agreement with the lanthanide contraction, the frequency distribution and values found for nitrato[28] and aqua[29] complexes.

Complete assignments are given in Table 4.

(*b*) $(ClO_2)_{0.33}La(ClO_4)_{3.33}$. The X-ray data of this complex and those obtained for $La(ClO_4)_3$ show some resemblance. A similar observation can be made for the IR and Raman vibrational data of these compounds [see Fig. 2(*a*)]. A first approach to the molecular structure of this complex can be made by writing it as the double salt $La(ClO_4)_3 \cdot 0.33Cl_2O_6$, as found with $(ClO_2)_{0.25}Sc(ClO_4)_{3.25}$ [in fact $Sc(ClO_4)_3 \cdot 0.25Cl_2O_6$][19] and $(ClO_2)_nCd(ClO_4)_n$ [$Cd(ClO_4)_2 \cdot nCl_2O_6$].[17] The

Table 4 Raman and infrared data (cm^{-1}) for $M(ClO_4)_3$ complexes (M = Y, La, Nd, Sm, Gd or Er). v = very, s = strong, m = medium, w = weak, br = broad and sh = shoulder

$Y(ClO_4)_3$		$La(ClO_4)_3$		$Nd(ClO_4)_3$		$Sm(ClO_4)_3$		$Gd(ClO_4)_3$		$Er(ClO_4)_3$		
Raman	IR	Raman	IR	Raman	IR	Raman	IR	Raman	IR	Raman	IR	Assignment
1305w	1262s	1287w	1258s	1245w	1250s		1256s	1311w	1258s	1298w	1267vs	$\nu(ClO_t)$
1248w	1232 (br)	1242w			1188 (br)		1105 (br)	1259w	1180m	1245w		
1047w	1018 (br)	1063m	1070 (br)	1058w	1057 (sh)	1052w	1036s	1083w	1025s (br)	1074w	1092 (sh)	$\nu_{asym}(ClO_b)$
1015m		1022m		1020m		1024m		1031m		1033w		
										1004m		
991vs	973s	982vs	985 (br)	987vs	968s	991vs	970 (br)	1000vs		986vs	974s	
635m	641s	631m	633 (br)	623m	630s	632m	627s	651 (sh)	639m	631m	640vs	$\nu_{sym}(ClO_b)$ $\delta_{asym}(ClO_b)$
	631s		620s	641 (sh)	622s			643m	619 (sh)		627s	
	619s				615s		610s		614s		616vs	
478m		465s		465m		475m		483m		475m		ρ_r
										463m		$+\delta_{sym}(ClO_b)$
						400w						$\nu_{sym} + \nu_{asym}$ [M–O(ClO_4)]
		290 (br)				361w						
		190w										Deformation M–O and lattice vibrations
		126w										

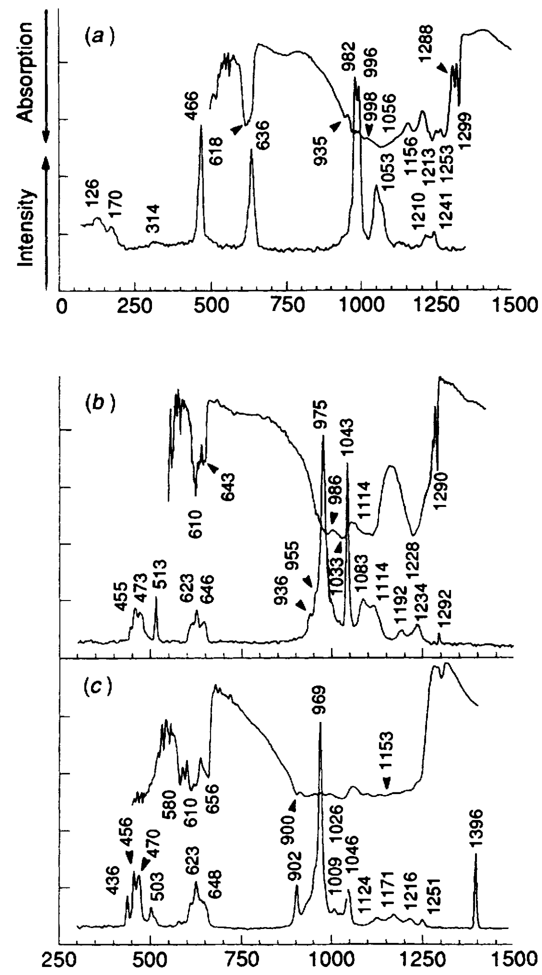

Fig. 2 Infrared and Raman spectra of $(ClO_2)_{0.33}La(ClO_4)_{3.33}$ (*a*), $ClO_2Er(ClO_4)_4$ (*b*) and $(NO_2)_3Er(ClO_4)_6$ (*c*)

Table 5 Vibrational bands (cm^{-1}) of $ClO_2Er(ClO_4)_4$ and $(NO_2)_3Er(ClO_4)_6$

$ClO_2Er(ClO_4)_4$		$(NO_2)_3Er(ClO_4)_6$		
Raman	IR	Raman	IR	Assignment
			3740w	$(\nu_{asym} + \nu_{sym})NO_2^+$
			2370s	$\nu_{asym}(NO_2^+)$
		1396m		$\nu_{sym}(NO_2^+)$
1292w	1290m			$\nu_{asym}(ClO_2^+)$
1234w	1228vs	1251w		$\nu_{asym}(ClO_t)$
1192w		1216w		$\nu_{sym}(ClO_t)$
1114s	1114m	1171w	1153 (sh)	
1083m		1124w		
1043vs				$\nu_{sym}(ClO_2^+)$
		1009w		$(\nu_{asym} + \nu_{sym})\ ClO_b + \nu_{sym}(ClO_4)$*
975vs	986 (sh)	969vs	969 (sh)	
955 (sh)	971 (sh)	950 (sh)		
936 (sh)		930 (sh)		
		902m	900 (br)	
646w	643m	648m	656s	ρ_r
623m		623m	610s	ρ_w
612w	610s		580s	$\delta(ClO_t)\ [+\delta(NO_2^+)]$
513m				$\delta(ClO_2^+)$
		503w		$\delta(ClO_b) + \rho_t$
473m		470m		
455m		456m		
		436w		

* NO_2ClO_4.

ClO_2^+ in Cl_2O_6 is characterised by bands and lines located in the IR at 1299–1288 cm^{-1} (ν_{asym} with isotopic ^{35}Cl–^{37}Cl splitting) and at 1053 cm^{-1} in the Raman (ν_{sym}). The $\nu_{sym}(ClO_4)$ vibration is assigned to the shoulder at 947 cm^{-1} on the Raman line and to the IR band at 935 cm^{-1}. The frequency and the low intensity of this line in the Raman and the medium intensity of the corresponding band in the IR indicate a high distortion of the ClO_4^- anion, and, given the splitting of the $\nu_{sym}(ClO_4)$ line around 990 cm^{-1}, this distortion appears also in the case of $La(ClO_4)_3$. The observed frequencies and the absence of splitting of the lines assigned to the deformation modes are therefore surprising. Another interpretation[21] based on previous results on $M(ClO_4)_{n+m}^{m-}$ anions, whereby the complex is considered as a definite salt $(ClO_2)_{0.33}La(ClO_4)_{3.33}$ in which the $La(ClO_4)_{3.33}^{0.33-}$ is a polymeric anion with bridging bidentate ClO_4 groups, is also possible. Here, for example, the following main assignments were made for the lines observed in the Raman spectrum for the stretching modes: 1241–1210, $\nu_{asym}(ClO_t)$; 1070, $\nu_{sym}(ClO_t)$; 996–982, $\nu_{sym}(ClO_b)$; 971–947 cm^{-1}, $\nu_{asym}(ClO_b)$.

(*c*) $ClO_2Er(ClO_4)_4$ *and* $(NO_2)_3Er(ClO_4)_6$. X-Ray data show that the $Er(ClO_4)_4^-$ anion appears in both complexes. The majority of bands and lines in the vibrational spectra of Fig. 2(*b*) and (*c*) are assigned to the vibrational modes of the anion, which

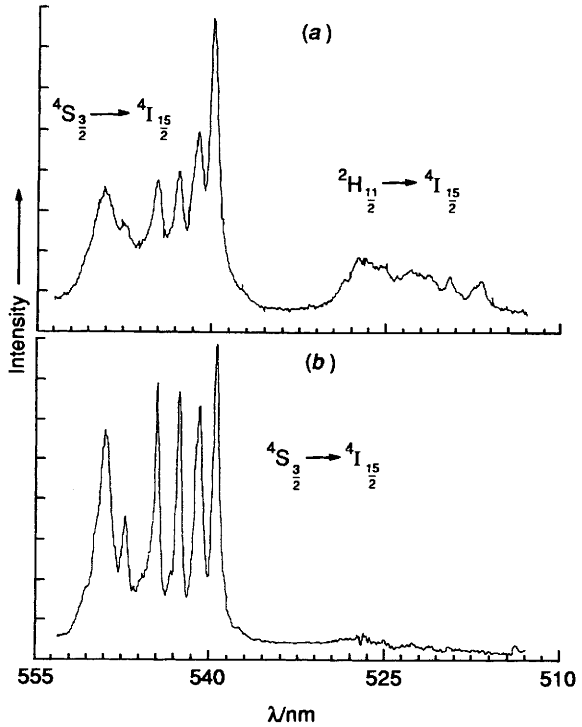

Fig. 3 Fluorescence spectra of $Er(ClO_4)_3$ at room temperature (*a*) and at 93 K (*b*) by excitation at 488 nm, $^4I_{\frac{15}{2}} \longrightarrow {}^4F_{\frac{7}{2}}$

can be considered as a polymeric chain with ClO_4 bridging bidentate groups.[8] A complete assignment is given in Table 5. Slight differences appear in frequencies and the splitting of bands in the spectra of the two compounds, depending on the anion–cation interactions which are higher with ClO_2^+ than NO_2^+. The assignment of bands and lines from ClO_2^+ and NO_2^+ cations and from ClO_4^- (in free NO_2ClO_4) are made as previously.[3,14]

Fluorescence phenomenon. Except for La^{III}, $4f^0$, and Lu^{III}, $4f^{14}$, 4f electrons in lanthanide(III) ions give rise to low-lying excited electronic states corresponding to visible absorption. The spin–orbit coupling interaction splits individual terms into J manifolds, which are themselves split into $2J + 1$ levels by the ligand field.[30] The relaxation of some excited states in most lanthanide ions results in light emission.[31] Laser-induced intense luminescence phenomena [10 to 50 times more intense than $\nu_{sym}(ClO_b)$ Raman lines] were detected with $Er(ClO_4)_3$.

Fluorescence spectra, presented in Fig. 3, have been recorded at room temperature (*a*) and at 93 K (*b*), when the 488 nm exciting line ($^4I_{\frac{15}{2}} \longrightarrow {}^4F_{\frac{7}{2}}$ transition) was used. At room temperature two groups of fluorescence lines at 545 and 526 nm are assigned to $^4S_{\frac{3}{2}} \longrightarrow {}^4I_{\frac{15}{2}}$ and $^2H_{\frac{11}{2}} \longrightarrow {}^4I_{\frac{15}{2}}$ relaxations respectively, the latter being formally forbidden. Its appearance at room temperature (as a broad and weak signal) probably results from thermal agitation, since it is no longer observed at 93 K, when the former ($^4S_{\frac{3}{2}} \longrightarrow {}^4I_{\frac{15}{2}}$) exhibits a fine structure characteristic of vibronic interactions.[32] Similarly, intense fluorescence phenomena were also observed with some of the other perchloratolanthanide complexes (Nd, Sm and Gd).

Conclusion

Once again Cl_2O_6 appears to be a very efficient perchlorating reagent. The use of vibrational spectroscopy and X-ray powder analysis has furthered the understanding of anhydrous perchlorato complexes. The family of layered compounds was extended and we have seen that bridging tridentate ClO_4 can appear with a nine-co-ordination around the metal. The report of an intense fluorescence for $Er(ClO_4)_3$ is a new phenomenon for a weak basic ligand.

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